

REMARKS

Claims 1-10, 12, 70-73 and 75-102 were presented for examination. All claims have been rejected under Section 103(a) as being unpatentable over WO 91/16409 and also over WO 85/02175.

The claims have been amended as described in the preceding pages. The basis for the amendment of the 14 to 19 carbon range is found on page 8, lines 19 to 20 and the basis for the 14 to 17 range is found in Table III, page 34. The basis for the amendment of the average number of branches range of 0.7 to 2.3 is found at page 4, line 19, and page 5, line 7 and the basis for the 0.7 to 2.1 range is found in claims 70 and 79. The basis for the 5-25% branching at the C₂ position range is found in claim 5. The basis for the 5% to 30% ethyl branching range is found in claims 1, 91 and 100. The basis for the quaternary carbon atom range is found in claims 1 and 80. The basis for the amount of methyl branching is found in original claim 9.

All of the claims of the present application have been amended to encompass a less broad class of alkyl sulfate/ethoxy sulfate surfactants. The average chain length per molecule is 14 to 19 carbon atoms, the average number of branches per molecule is 0.7 to 2.3, the amount of methyl branches must be at least 40 percent of the branches and from 5 to 25 percent of the number of branches are on the C₂ atoms of the composition.

WO '409

The Examiner asserts that the claims are obvious in view of WO '409 because it teaches that the commercially available sulfate, Lial 125, is biodegradable and branched. The Examiner's position that in view of this and in absence of showing to the contrary, one of ordinary skill in the art would reasonably construe the sulfates of the reference to encompass the claimed sulfates. The Applicants previously submitted a Declaration Under Rule 132 which contained data showing that a similar Lial product gave a much lower multisebum detergency than the branched fraction of a Neodol 45 alcohol sulfate. The Examiner held that the Declaration "is not commensurate in scope with the claimed invention." The Examiner further stated that "Applicant claims a broad class of alkyl sulfate/ethoxy sulfate surfactants such as biodegradable sulfate" as described in claim 1, Applicant's most comprehensive claim but "the Declaration compares a very narrow and specific branched fraction Neodol 45 alkyl sulfate with the prior art alkyl sulfate." It is

the Examiner's position that one of ordinary skill in the art would not have been able to determine the criticality of the showing in view of the Applicant's Declaration not being commensurate in scope to the claimed invention.

The Applicants submit the enclosed Declaration Under Rule 132 from William Warren Schmidt to prove that the invention as claimed in the amended claims is nonobvious. This declaration describes experiments which were carried out with a Neodol 45 sulfate and sulfates of a C₁₄ branched alcohol and two different C₁₄₋₁₅ branched alcohols. All of the alcohols were prepared by skeletal isomerization of the described internal olefins according to the procedure described in Example 5 of the present application. Two of the sulfates had a branching index of 0.92 and 0.94 and the third had a branching index of 1.03. All have methyl branching, ethyl branching, and branching at the C₂ position with the scope of the amended claims.

The multisebum detergency was determined for the Neodol 45 sulfate and the branched alcohol sulfates according to the procedure described in the present application. The experiments described in the previous Rule 132 Declaration and in this application were carried out more than 10 years ago. A slightly different multisebum soil has been obtained since that time. In general, it has been determined that this multisebum soil results in a slightly lower detergency level than the old multisebum soil used in the experiments described in the previous Rule 132 Declaration and in this application.

It can be seen that the multisebum detergency for the Neodol 45 sulfate was determined to be 10.6. The detergencies for the branched C₁₄ and the two branched C₁₄₋₁₅ alcohol sulfates were determined to be 25.1, 27.9 and 26.3. These results cannot directly be compared with the results from the previous Rule 132 Declaration and the examples in the present application because of the difference in the multisebum soil and because the level of surfactant used in the present experiments was higher--0.4 grams per liter. The least significant difference at 95 confidence level is about 2 for these experiments. As discussed below, the Applicants believe that this data shows that there is a significant difference in the detergencies of the branched alcohol sulfates within the scope of the claims of the present invention and the prior art composition.

The data shown in the previous Declaration clearly proves that a branched alcohol sulfate provided a considerably higher multisebum detergency than the Neodol 45 alcohol sulfate it was compared against (35.5 versus 15.8). The detergency of the Lial 145 alcohol sulfate was only

slightly better than that of the Neodol 45 alcohol sulfate (18.5 versus 15.8). The data in the experiments provided in the present Rule 132 Declaration shows that sulfates of branched alcohols within the scope of the claims of the present invention give much better multisebum detergencies than the Neodol 45 alcohol sulfate. Thus, it is reasonable to conclude that the branched alcohol sulfates of the present invention give a much better detergency than Lial 145 alcohol sulfate. Since that material is very similar to the product described in WO '409, it is reasonable to conclude that sulfates of branched alcohols within the scope of the amended claims would likewise give superior detergencies than the product described in WO '409.

The Applicants assert that the data provided in the two Rule 132 Declarations and provided in the specification itself provide a sufficient showing that branched alcohol sulfates within the scope of the claims, as amended, of the present invention give an unexpectedly higher level of multisebum detergency than products such as disclosed in the WO '409 reference. For this reason, the Applicants assert that the Declarations overcome the rejection based on this reference.

WO '175

The Examiner has also maintained the rejection based on WO '175. This reference is said to disclose a detergent composition wherein the compositions comprise C₁₄ alcohols having branching at the 2- position and an additional methyl branch. The Examiner admits that the reference lacks the present specific teaching of branches per molecule but concludes that it would have been obvious to one of ordinary skill in the art to expect similar characteristics and properties from the sulfated alcohols of the reference and that "absence a showing to the contrary," that a prima facie case of obviousness was made.

The Applicants assert that the data presented in the new Rule 132 Declaration and the previous Rule 132 Declaration provide "a showing to the contrary" and show that the compositions claimed in the amended claims do provide a significant unexpected advantage over prior art compositions such as those described in WO '175.

The record reflects that the Examiner's primary argument for making the present rejections is the assertion by the Examiner that WO '175 discloses a C₁₄ alcohol that is structurally similar to the presently claimed compositions. Applicants respectfully submit that the Examiner's "structural similarity" rationale cannot support prima facie obviousness rejections

of the present claims over WO '175. First, the branching at the 2-position contains five carbons and is not methyl and ethyl within the scope of the amended claims (see p. 8).

Before discussing the inapplicability of the “structural similarity” obviousness rationale in the present application, Applicants note that even assuming *arguendo* that this “structural similarity” obviousness analysis is appropriate and further assuming *arguendo* that WO '175 discloses, as asserted by the Examiner, an isomer of the presently claimed compositions, these assumed facts would not automatically be conclusive proof of *prima facie* obviousness. MPEP 2144.09 states:

**HOMOLOGY AND ISOMERISM ARE FACTS WHICH
MUST BE CONSIDERED WITH ALL OTHER RELEVANT
FACTS IN DETERMINING OBVIOUSNESS**

Compounds which are position isomers (compounds having the same radicals in physically different positions on the same nucleus) . . . are generally of sufficiently close structural similarity that there is a presumed expectation that such compounds possess similar properties. . . .

Isomers having the same empirical formula but different structures are not necessarily considered equivalent by chemists skilled in the art and therefore are not necessarily suggestive of each other. *Ex parte Mowry*, 91 USPQ 219 (Bd. App. 1950) (claimed cyclohexylstyrene not *prima facie* obvious over prior art isohexylstyrene). Similarly, homologs which are far removed from adjacent homologs may not be expected to have similar properties. *In re Mills*, 281 F.2d 218, 126 USPQ 513 (CCPA 1960) (prior art disclosure of C₈ to C₁₂ alkyl sulfates was not sufficient to render *prima facie* obvious claimed C₁ alkyl sulfate).

Homology and isomerism involve close structural similarity which must be considered with all other relevant facts in determining the issue of obviousness. . . . Homology should not be automatically equated with *prima facie* obviousness because the claimed invention and the prior art must each be viewed “as a whole.” . . .

(emphasis added and citations omitted).

Applicants first note that the compound of WO '175 and the claimed compositions are not, as the Examiner seems to suggest, position isomers as defined above in the quote from MPEP 2144.09 because position isomers according to MPEP 2144.09 are “compounds having the same radicals in physically different positions on the same nucleus.” As

discussed in detail below, such similarities do not exist in the present case. More importantly, based on MPEP 2144.09, if it is assumed *arguendo* that a “structural similarity” obviousness analysis is appropriate in the present case and if it is further assumed *arguendo* that WO ‘175 discloses, as asserted by the Examiner, an isomer of the presently claimed compounds, the assumed isomerism would be only one factor out of many factors to be considered in the determination of obviousness. The Examiner still must consider an invention as a whole. Therefore, the Examiner must consider all of the limitations of the present claims (for example, limitations relating to branching) and must not simply ignore all of the limitations not disclosed by WO ‘175. Applicants respectfully submit that a bare assertion that one isomer renders all other isomers obvious is inappropriate.

No Prima Facie Case for Obviousness has Been Established

As previously mentioned, Applicants respectfully assert that the Examiner’s “structural similarity” arguments cannot support *prima facie* obviousness rejections of the present claims over WO ‘175. Applicants submit that the “structural similarity” obviousness analysis is applicable only in situations wherein prior art discloses structures that are very close to claimed structures. Applicants point out that the title of MPEP 2144.09 is “Close Structural Similarity Between Chemical Compounds (Homologs, Analogues, Isomers)” (emphasis added) and that the first statements within that section are as follows:

**REJECTION BASED ON CLOSE STRUCTURAL
SIMILARITY IS FOUNDED ON THE EXPECTATION
THAT COMPOUNDS SIMILAR IN STRUCTURE WILL
HAVE SIMILAR PROPERTIES**

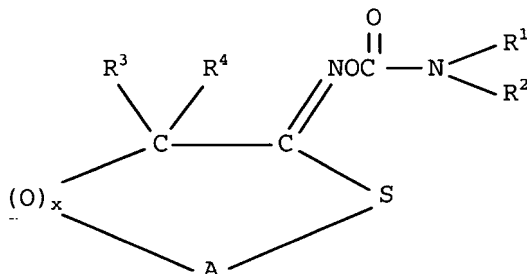
A prima facie case of obviousness may be made when chemical compounds have very close structural similarities and similar utilities.

(emphasis added).

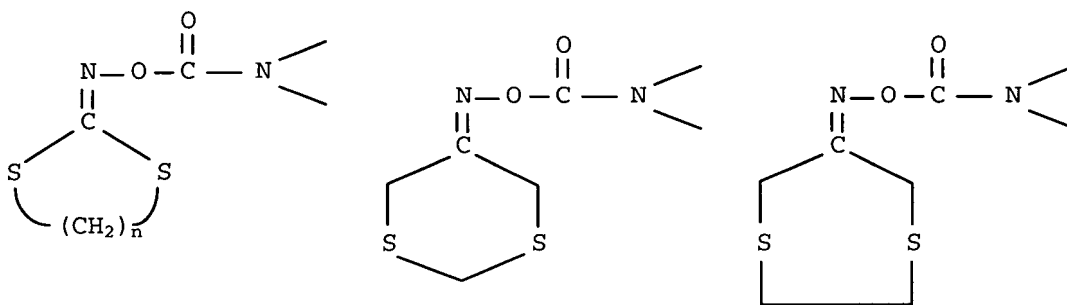
To illustrate the Applicants’ position on the meaning of “very close structural similarity,” without commenting on the correctness or currency of other holdings or discussions therein, Applicants refer to the cases cited by the Examiner in rejecting the present claims based on structural similarity: *In re Payne*, 606 F.2d 303, 203 USPQ 245 (CCPA 1979); *In re Papesch*, 315 F.2d 381, 137 USPQ 43 (CCPA 1963); *In re Dillon*, 919 F.2d 688, 16 USPQ2d 1897 (Fed. Cir. 1991). In each of these cases, specific molecular structures (individual molecule graphically

illustrated, specifically named, or represented by formula, etc.) capable of bond-by-bond and atom-by-atom comparison were present both in the claims and in the prior art upon which “close structural similarity” obviousness rejections were based.

For example, in *In re Payne*, 606 F.2d 303, 203 USPQ 245 (CCPA 1979), claim 1 recited the structural formula:



“Structural similarity” obviousness rejections under appeal had been based upon prior art disclosing the following structures:



In all of the cases cited by the Examiner in support of the Examiner’s structural obviousness rejections, the distinct structural similarities and differences between the prior art in those cases and the claims of those cases were clearly and readily capable of visualization, characterization, and enumeration. Applicants assert that the “structural similarity” obviousness analysis is most readily applicable in these types of situations where both prior art and claims show specific molecular structures (individual molecule graphically illustrated, specifically named, or represented by formula, etc.). Bond-by-bond and atom-by-atom comparisons inherently conducted in such situations make it possible to determine whether molecular structural similarities are extremely numerous and molecular structural differences are very insignificant, such as where the types of molecular structural differences present are well-known to tend to have no significant effect upon molecular properties. In instances of extremely

numerous structural similarities coupled with very insignificant differences, it might be said that one of ordinary skill in the art would be motivated to arrive at claimed compounds by making insignificant modifications to known prior art compounds, retaining in the modified compounds most of the structural features of the original known compounds. The motivation to make the insignificant modifications while retaining most other structural features is based upon the desire to create modified compounds having the same properties as the original known prior art compounds. One of ordinary skill in the art would expect the properties of insignificantly modified compounds to be the same as properties of the known prior art compounds if the structural similarities between the modified and known compounds are numerous enough.

This reasoning is based on numerous molecular structural similarities coupled with very insignificant molecular structural differences. If these factors are present, very insignificant differences can be ignored, under appropriate circumstances, as obvious modifications. Absent sufficiently numerous specifically identifiable similarities or in the presence of differences that are not insignificant, Applicants contend that the differences should not be ignored. The "structural similarity" obviousness analysis should be reserved for situations involving very close structural similarities (MPEP 2144.09), and in all other instances the Examiner must point to teachings or suggestions of each and every limitation of the claims.

In asserting obviousness in the present application, the Examiner has made and relied upon general assertions of "structural similarity," but the Examiner has not pointed to very close and numerous structural similarities between the presently claimed compositions and compositions of WO '175. The general assertion of structural similarity made by the Examiner is limited to "because they are the same compounds but different isomers" (no showing of why this is so) certainly cannot be said to rise to the level of numerous structural similarities typically observed when known and claimed specific molecular structures (individual molecule graphically illustrated, specifically named, or represented by formula, etc.) have been compared in a bond-by-bond and atom-by-atom fashion and found to be obvious variants of each other. Furthermore, the differences between compositions of WO '175 and the present claims, which differences have been ignored by the Examiner, are not insignificant. The Examiner has ignored limitations of the present claims which are not well-known in the art to have little effect on properties.

The branched alcohols described in the reference are all 2-alkyl branched compounds. They have to be by virtue of the description in the application on pages 4 through 7 and also by the description of the process for making these materials, for example, at page 23. See also Table 3 on page 38 wherein all of the isomers shown are 2-alkyl branched alcohols.

Furthermore, the branches which extend from the 2 position on the chain must also be higher alkyl chains than just methyl or ethyl. The description of these alcohols shown on page 6 requires that the branch have 5 carbon atoms. This is the primary product of the invention of the reference. Claim 1 describes the branch as having from 3 to 6 carbon atoms. Obviously, this is not methyl or ethyl.

Attached hereto as Attachment A is a report of additional experiments that were done and submitted to the PCT Examiner in 1998. 2-alkyl branched alcohols having 14, 15, and 16 carbon atoms were made with methyl, ethyl, propyl, butyl, or hexyl branches. Sulfates of these materials were made and tested according to the procedure described to determine multisebum soil removal and triolein soil removal. All of the experiments which can be compared directly show that better results in terms of soil removal are achieved with methyl or ethyl groups than can be achieved with propyl, butyl, or hexyl groups.

This data shows that "very close structural similarity" does not exist in this case since the reference describes 100 percent 2-alkyl branching with long chains and the present invention describes mostly shorter chain branching wherein only 5 to 25% of the branches are at the 2 position. This means that compositions of the present invention cannot have 100 percent branching at the C₂ position.

The reference does not describe materials such as those that are claimed in the present application and thus it cannot suggest that improved soil removal could be achieved by modifying the longer chain 100 percent C₂ position branched alcohols described therein by reducing the C₂ branching to as little as 5 percent and having only mostly lower chain branches.

The inventors herein were honored for this invention at the Southwest Regional Industrial Innovation Awards Program Symposium of the American Chemical Society. The Applicants submit this as evidence of commercial success which rebuts a case of prima facie obviousness. A copy of the announcement is attached hereto as Attachment B. A copy of the presentation which was given at the Awards Ceremony is also enclosed herewith as Attachment

C. The presentation contains several slides which are relevant to the question of whether or not the differences between the alcohols of the reference and the presently claimed alcohols are "significant" in that whatever structural similarity exists between the two sets of alcohols is not sufficient to predict the properties of the presently claimed alcohols from what is known about the alcohols of the reference.

Slide 16 relates to the Krafft temperature of selectively branched alcohol sulfates within the scope of the present claims (the top 3 alcohols in the slide), sulfates of alcohols which have almost all ethyl or methyl branching at the C₂ position (the fifth and sixth alcohols in the slide), and the sulfate of one linear C₁₆ alcohol (the last alcohol in the slide). The Krafft temperature is the temperature at which the mixture containing the alcohol sulfates becomes clear and is an indication of solubility. Since cold water detergency is one of the goals of the present invention, it is better when the Krafft temperature is lower. As can be seen, all three of the selectively branched alcohol sulfates of the present invention have considerably lower Krafft temperature than the sulfates where almost all of the branching is 2-ethyl or 2-methyl (which are most akin to the alcohol sulfates described in the reference). This is another indication that the previously discussed differences in structure between the alcohol of the reference and the presently claimed alcohol do make a significant difference and that the properties of sulfates of the present invention cannot be predicted from the disclosure of the reference.

Slide 17 shows another physical property difference between the branched alcohol sulfates. The calcium tolerance of the branched alcohol sulfates of the present invention is much higher than the calcium tolerance of the 2-ethyl and 2-methyl branched alcohol sulfates. Slide 19 clearly shows that the detergency performance (at 10°C and 150 ppm water hardness) of the branched alcohol sulfates of the present invention is much better than the detergency performance of the 2-ethyl branched alcohol sulfate and the linear alcohol sulfate (more data that supports the nonobviousness of this invention). This data also shows that the structural differences between the two sets of alcohols give different physical properties and that the properties of the sulfates of the present invention cannot be predicted from the disclosure of the reference.

A portion of this data appears in the article "Solution and Performance Properties of New Biodegradable High-Solubility Surfactants" in Tables 8, 9 and 11 wherein branched

alcohol sulfates of this invention are referred to as random methyl alcohol sulfates (RMC15, RMC1617, RMC18). This article, which is enclosed herewith as Attachment D, was published as part of the proceedings of the 5th World Surfactants Congress in 2000.

Another slide on detergency performance of these alcohol sulfates which was not part of the presentation (which is also enclosed herewith as Attachment E) includes detergency performance data for alcohol sulfates which contain almost 100 percent either 2-hexyl, 2-butyl, 2-ethyl, or 2-methyl branching. Looking at this slide, it can be seen that the C₁₅ and C_{16, 17} alcohol sulfates have greatly enhanced detergency performance as compared to the branched alcohol sulfates which have almost 100 percent branching at the C₂ position and particularly much better detergency performance than the 2-hexyl and 2-butyl branched alcohol sulfates. The C₁₈ selectively branched alcohol sulfate also had better detergency performance than all of the others but the difference is not quite as dramatic. Again, this data shows that the structural differences between the branched alcohol sulfates result in different physical properties which cannot be predicted.

Very close structural similarity does not exist in this case and very close structural similarity is required for the analysis applied by the Examiner in the present rejections. It is insufficient for the Examiner to rely on broad assertions that the claimed compositions and the compositions of WO '175 generally fall within the same class or are generally related.

Therefore, the guidelines associated with very close structural similarity should not be applied to the present claims, and there is no justification for ignoring differences between the present claims and compositions of WO '175. No prima facie case for obviousness has been established.

No Suggestion or Teaching of the Claim Limitations is Shown

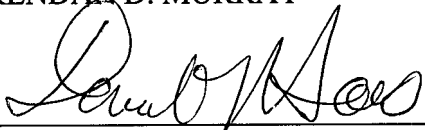
No obvious modification of the compositions of WO '175 would result in a composition that satisfies each and every limitation of the present claims. Only major modifications of the compositions of WO '175 could result in a composition characterized by each and every limitation of the present claims. Furthermore, WO '175 contains no suggestion that would lead a person of ordinary skill in the art from the compositions of WO '175 to the compositions characterized by each and every limitation of the present claims. The only way that a person of ordinary skill in the art, beginning with WO '175, would be motivated to arrive

at a composition satisfying each and every limitation of the present claims is by using the present claims as a blueprint and engaging in impermissible hindsight reconstruction.

For these reasons, the Applicants assert that this rejection has been overcome.

Respectfully submitted,

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and BRENDAN D. MURRAY

By 

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Attachment A

TH-0681 PCT, Report of additional experiments

2-Alkyl branched alcohols, having a total of 14, 15 and 16 carbon atoms respectively including their alkyl branches which were methyl, ethyl, propyl, butyl or hexyl, were purchased and used. All branched alcohols were characterised by ^{13}C NMR and found to be greater than 97 % pure. All alcohols were converted to alcohol sulphate sodium salts with ClSO_3H followed by neutralisation with NaOH , as described in Example 6 of the application.

The branched alcohol sulphates were subjected to detergency tests using the laboratory radiotracer detergency procedure of W.T. Shebs and B.E. Gordon, J. Am. Oil Chem. Soc., 45 (1968) 377 and J. Am. Oil Chem. Soc., 46 (1969) 537, as described on pages 8-11 of the application. The branched alcohol sulphates were tested against multisebum or triolein soiled permanent press 65/35 polyester/cotton (PPPE/C) fabric. The formulation in each case was 0.2 g/L alcohol sulphate, 0.34 g/L builder (Zeolite-4A) and 0.2 g/L Na_2CO_3 .

The results, expressed as % soil removal, are presented in the following Tables 1 and 2.

Table 1

Effect of 2-alkyl branched alcohol sulphates on multisebum soil removal

Branching	<u>15-Carbon alcohol sulphate</u>		<u>16-Carbon alcohol sulphate</u>	
	tested at 10 °C	tested at 32 °C	tested at 10 °C	tested at 32 °C
Methyl	17.6	---	17.6	38.3
Ethyl	---	---	14.0	34.1
Propyl	12.4	31.1	---	---
Butyl	---	---	6.7	32.9
Hexyl	4.0	7.3	7.5	13.4

LSD₉₅ (Least Significant Difference at 95% probability) is 2.0 at 10 °C and 4.8 °C at 32 °C

Table 2

Effect of 2-alkyl branched alcohol sulphates on triolein soil removal

Branching	<u>14-C alcohol sulphate</u>		<u>15-C alcohol sulphate</u>		<u>16-C alcohol sulphate</u>	
	at 10 °C	at 32 °C	at 10 °C	at 32 °C	at 10 °C	at 32 °C
Methyl	---	---	---	---	21.4	34.7
Hexyl	3.5	5.2	4.8	13.2	7.5	16.0

LSD₉₅ (Least Significant Difference at 95% probability) is 4.3 at both temperatures

59th Southwest Regional Industrial Innovation Awards Program

October 25 – 28, 2003
Oklahoma City, OK

Honoring Successful Innovations from the Chemical Enterprise



Because the innovations of industry are essential to a healthy economy, the American Chemical Society's (ACS's) Industry Member Programs has instituted the Regional Industrial Innovation Awards Program. The program recognizes individuals and teams for their creative innovations that have resulted in a commercial product or process. This awards program also highlights the outstanding contributions that the profession of chemistry has given to society, as well as the corporate leadership that encouraged the dissemination of knowledge that is facilitated in these innovations.



The recipients of the 59th Southwest Regional Industrial Innovation Awards Program are **Mr. Louis Kravetz, Dr. Brendan D. Murray, and Dr. David M. Singleton** (Shell Chemical LP, Houston, TX) for developing a new class of high solubility, biodegradable alcohol-based surfactants with selective and controlled degrees of branching for use in cold water washing processes.

Mr. Louis Kravetz joined Shell Chemical Co. in 1963 after receiving his M.S. in chemistry from the Brooklyn Polytechnic Institute. During his 35 year career at Shell, he worked at three different research facilities – Union Labs, NJ, Emeryville, CA, and Westhollow Technology Center, Houston, TX. During this time, he has worked on applications research in textiles, hydrogen peroxide, glycerine, ethylene glycol, and surfactants. Mr. Kravetz is the recipient of 14 U.S. patents and is the author of 34 technical publications.

Dr. Brendan D. Murray received his B.A. in chemistry from the University of California, Santa Cruz in 1980 and his Ph.D. in inorganic chemistry from the University of California, Davis in 1984. He joined Shell Development Co., Houston, TX in 1985 and was an exchange scientist from 1995–1996. Dr. Murray returned to Shell's Westhollow Technology Center in Houston, TX in 1996 and continued to develop new commercial applications for catalysis where he is currently the Catalyst Opportunity Development Strategist. He is the recipient of 26 U.S. patents and has authored over twenty technical presentations.

Dr. David M. Singleton received his B.S. in chemistry from Queen Mary College, London University in 1960, his Ph.D. in physical-organic chemistry from McMaster University in Hamilton, Ontario in 1965, and his postdoctoral studies at Case Institute of Technology in 1967. Dr. Singleton joined Shell Development Co., Emeryville, CA in 1967 and was an exchange scientist in Amsterdam, The Netherlands from 1975–1976. Dr. Singleton returned to Shell's Westhollow Technology Center in 1976 where he worked on a number of challenging issues in the areas of catalysis and household detergents. Dr. Singleton retired from Shell in 1999 after 32 years.

Join us in honoring Mr. Kravetz, Dr. Murray, and Dr. Singleton. The program will include a symposium in which the honorees will present his outstanding work and an awards ceremony in which the honorees will be formally recognized. This industrial-focused event also presents a significant networking opportunity for ACS members, industrial researchers, corporate leaders, and students.

Symposium

Monday, October 27, 2003
(Time/Location – TBD)

Awards Ceremony

Monday, October 27, 2003
6:30 – 8:30 p.m.
(Location – TBD)

Attachment C



Shell Chemicals

The Development and Commercialization of Biodegradable Selectively Branched Detergent Alcohols

Louis Kravetz, David Singleton and Brendan Murray*
Shell Chemical LP
Westhollow Technology Center
Houston, TX 77082



Shell Chemicals

Surfactants

Multi-million ton/ year global business

Anionic surfactants are the largest group

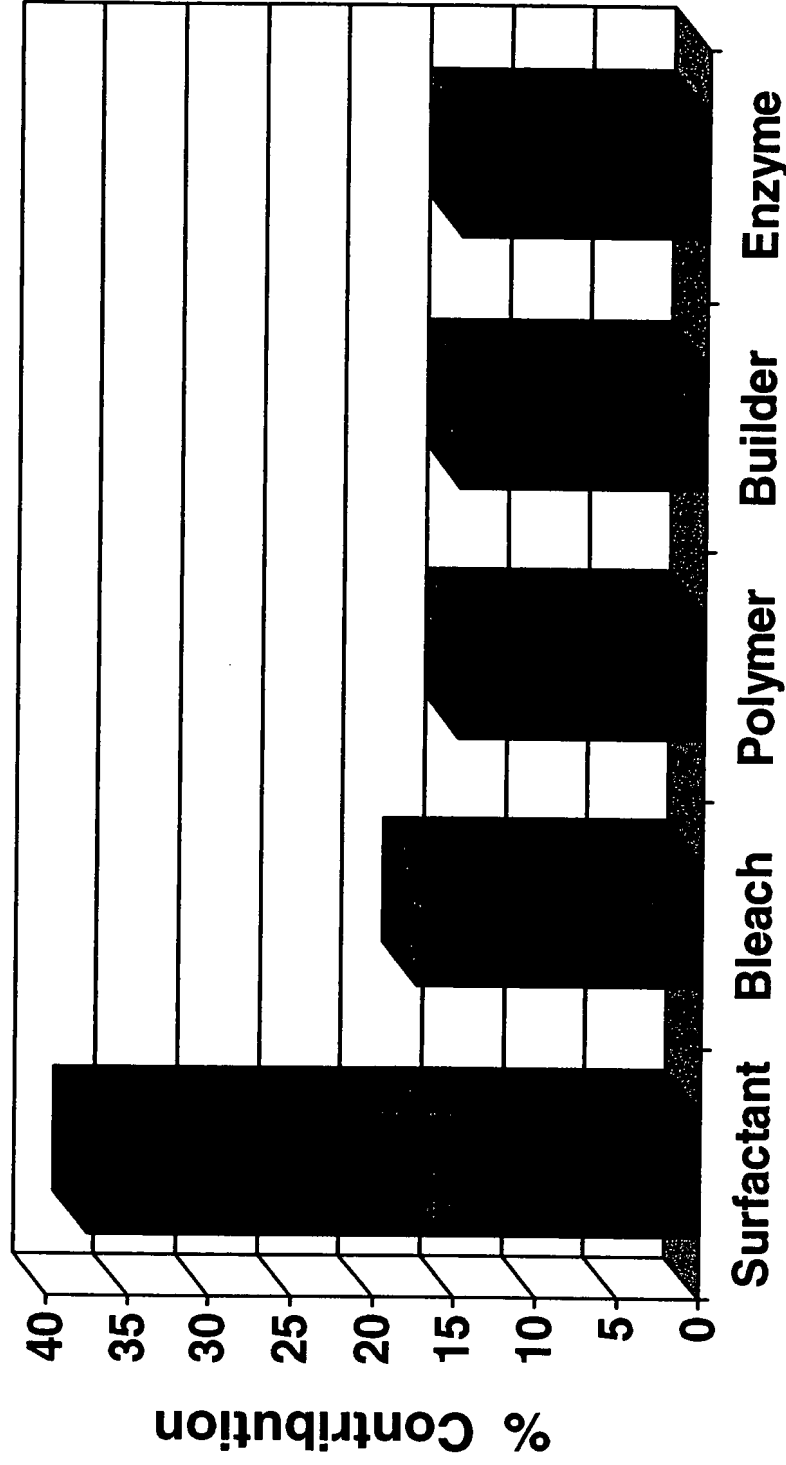
They wet fabrics and soils; remove dirt and stains

The single most important cleaning ingredient in most laundry and household cleaning products



Shell Chemicals

Performance Contribution to Detergency

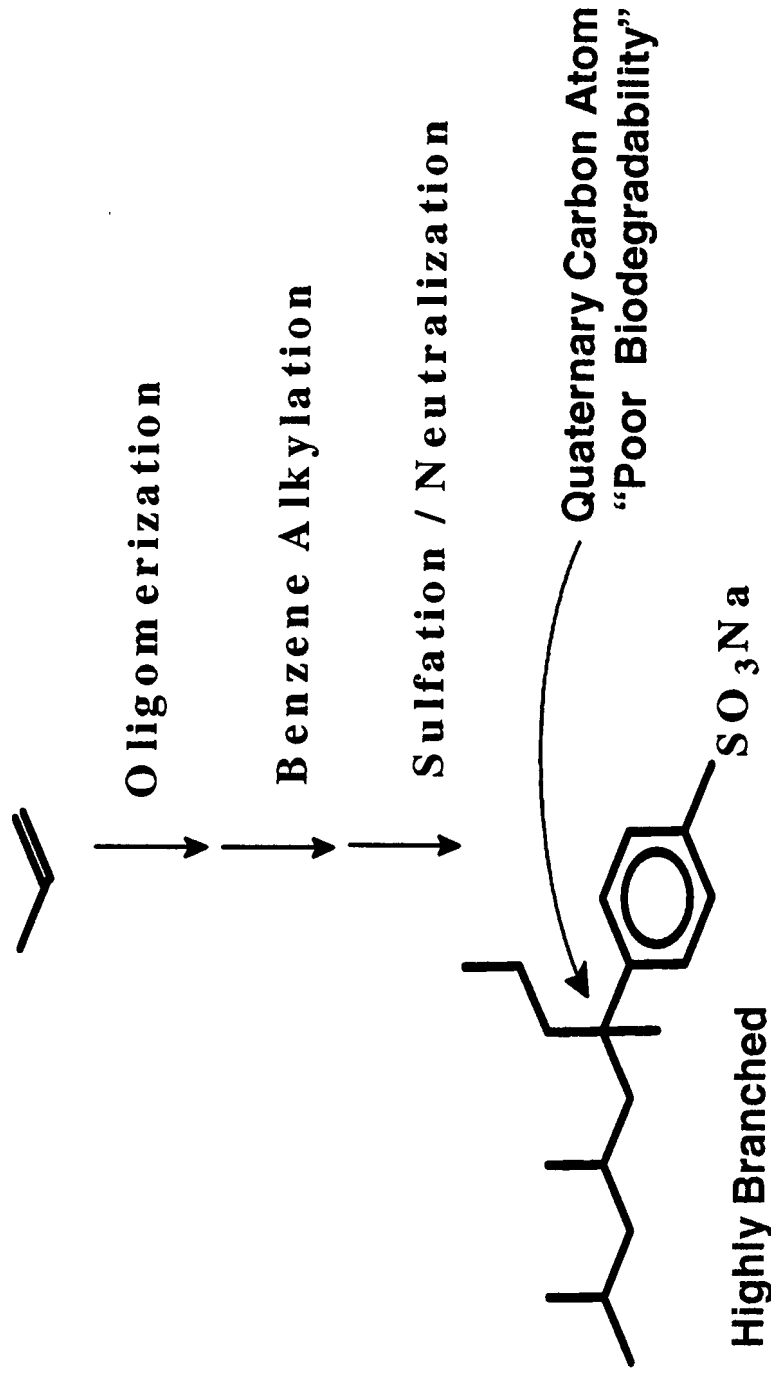


* G. Baillely et al., *Proceedings of the 5th World Conference on Detergents*, (2003)



Shell Chemicals

1950's Vintage Alkylbenzene Sulfonate





Surfactant Events – A Need for Innovation

1950's - Highly Branched Alkylbenzene Sulfonates, (ABS)

slow biodegradation, foaming, aquatic toxicity?

1960's – ABS Regulation begins – Rapid replacement by Biodegradable Linear Alkylbenzene Sulfonates, Linear Alcohol Sulfates and Linear AES

A Paradigm is born: “*Alkyl branching is Bad*”

1970's - Movement to lower wash temperatures creates a need for better cold water detergency

1980's *The Alkyl Branching Paradigm is Challenged*

2000's - High Solubility Biodegradable, Selectively Branched Detergents are commercialized



Recent Trends in Washing Processes

- Lower Wash Water Temperature
- Lower Energy Consumption
- Shorter Wash Times
- Reduced Water Usage

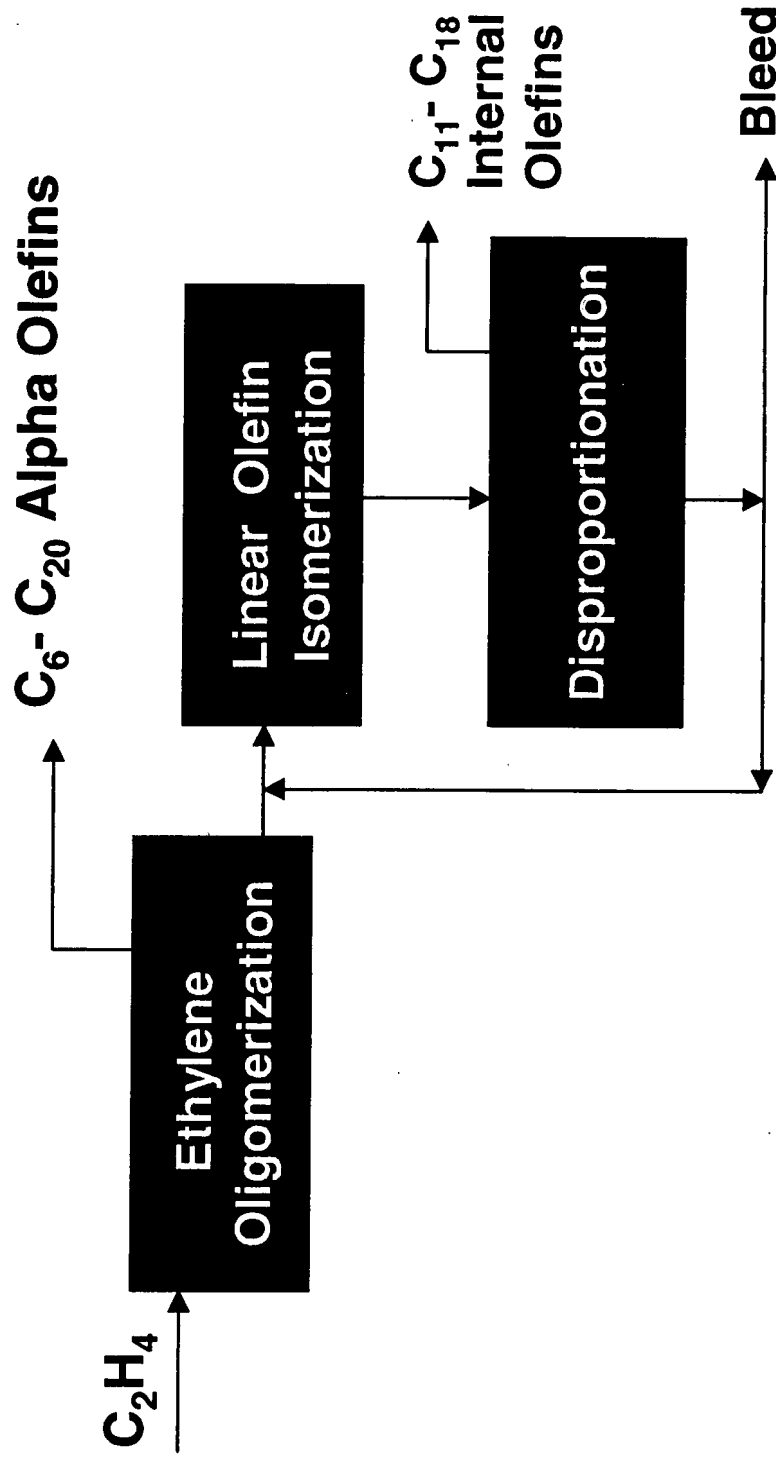


Shell Chemicals

Desired Surfactant Properties

- **Excellent Surface Activity**
- **Readily Biodegradable**
- **Superior Cold Water Detergency**
- **Improved Hard Water Solubility**
- **Ability to use Less Surfactant**
- **Affordable and Consistent Production**

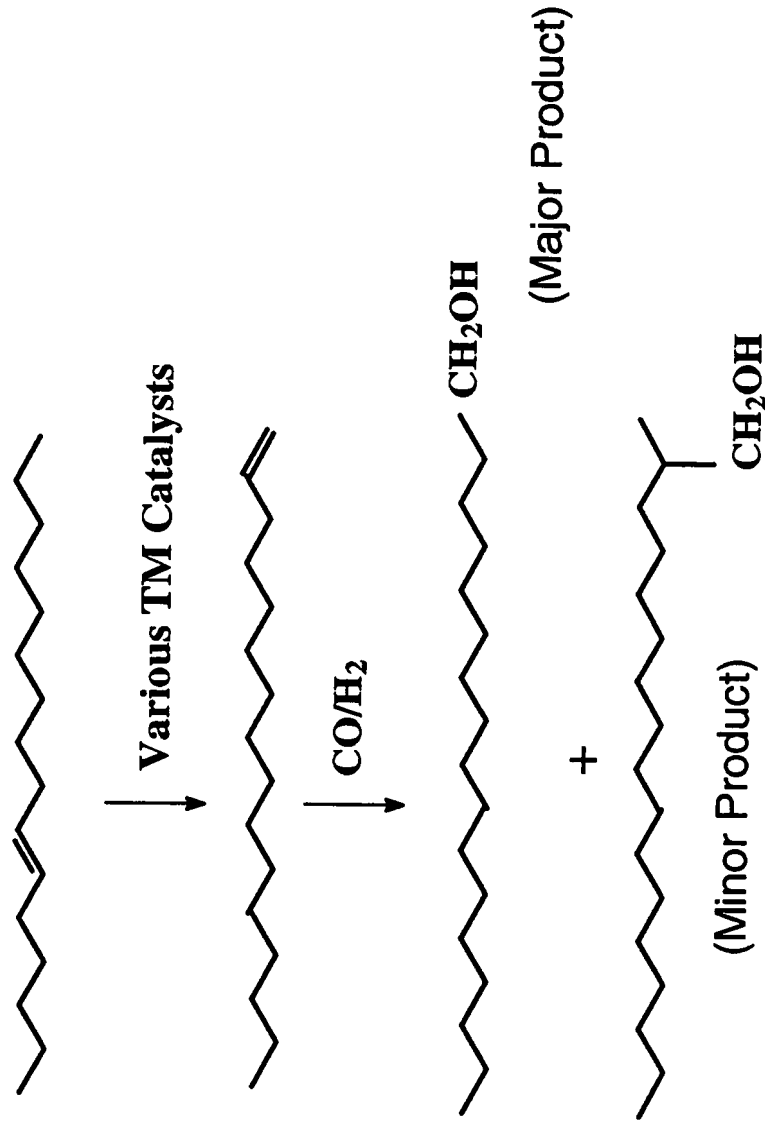
Shell Higher Olefins Process (SHOP)





Shell Chemicals

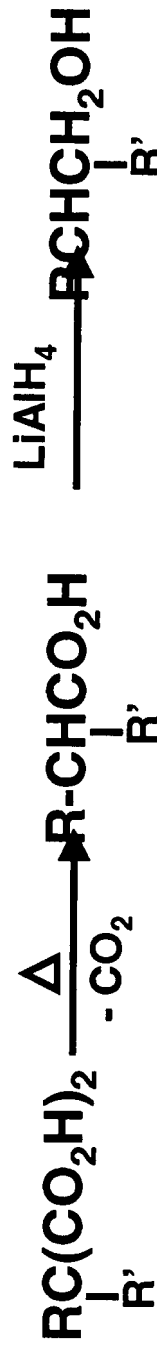
Shell Hydroformylation Process (SHF)





Model Compound Studies

Malonic Ester Synthesis of 2-Alkyl Branched Alcohols



Alcohols were converted to the alcohol sulfate sodium salts by treatment with ClSO_3H , followed by neutralization with NaOH

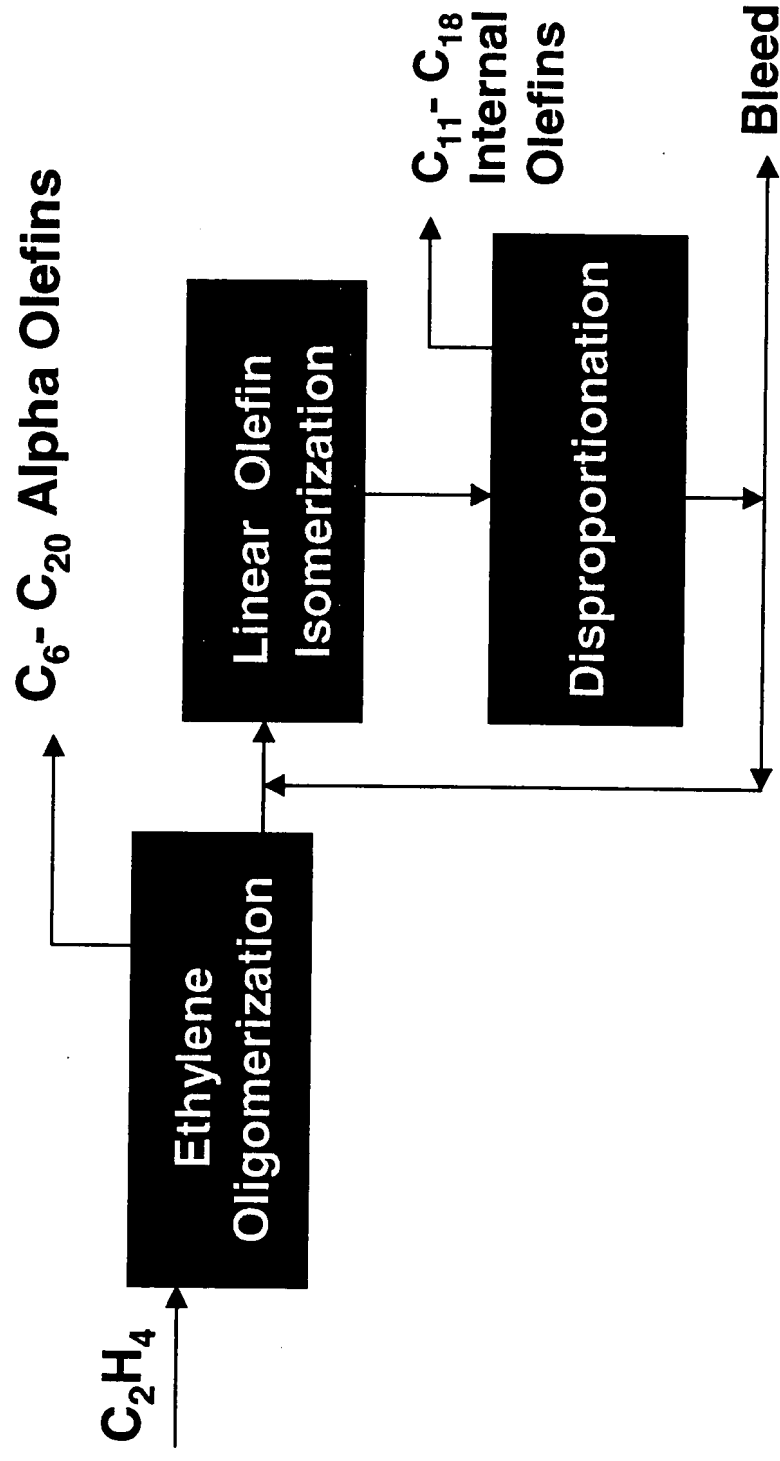
How to Introduce Controlled Branching

- **Controlled Dimerization / Oligomerization of Lower Olefins**
- **Cross Metathesis Schemes**
- **Selective Skeletal Isomerization of Linear Olefins**
 - Use a proprietary, “pore engineered” zeolite catalyst
 - Makes mainly mono-branched olefins with the alkyl groups distributed at beneficial positions along the backbone
 - Very low level of quaternary carbon atoms in product



Shell Chemicals

Shell Higher Olefins Process (SHOP)





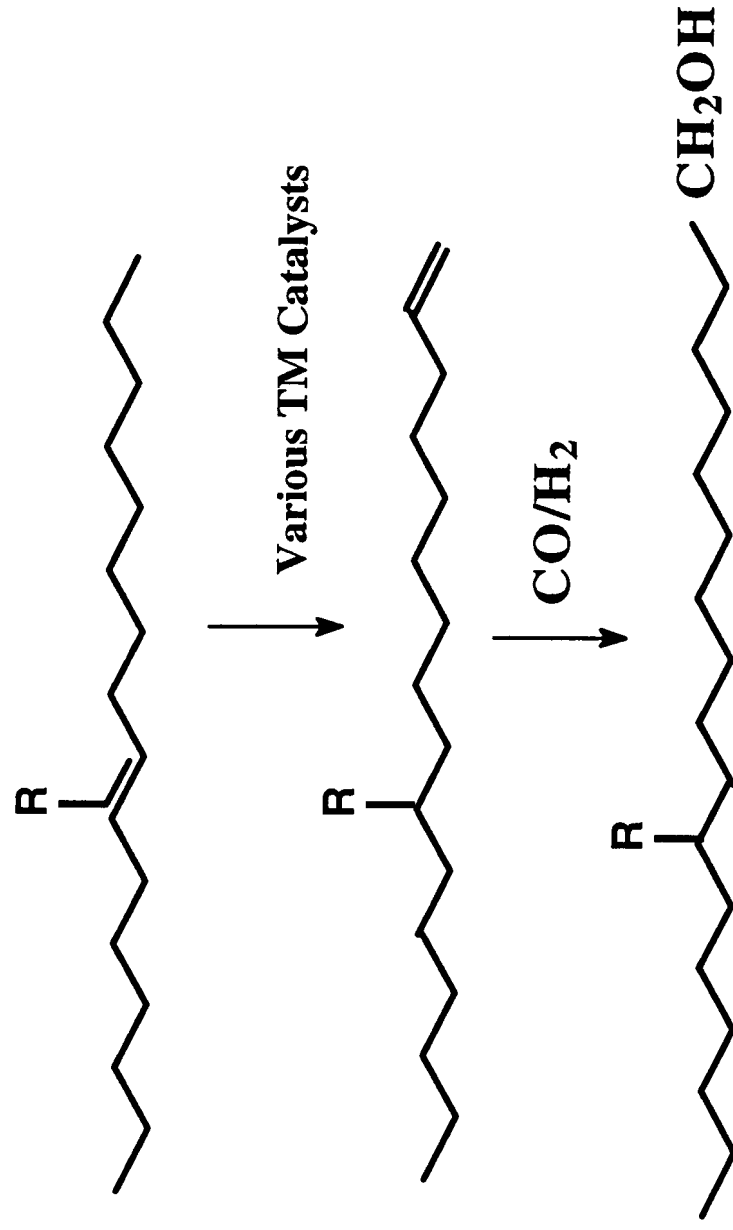
Skeletal Olefin Isomerization Process

- **Uses Alpha or Internal Olefins as Feedstocks**
- **Low Severity Operation**
- **Thermodynamic Equilibrium Conversion (>95%)**
- **Very High Selectivity (>98%)**
- **Multiply Regenerable Zeolite Catalyst**
- **Fully Compatible with the SHOP and SHF Processes**
- **Very High Catalyst Turnover Rate**



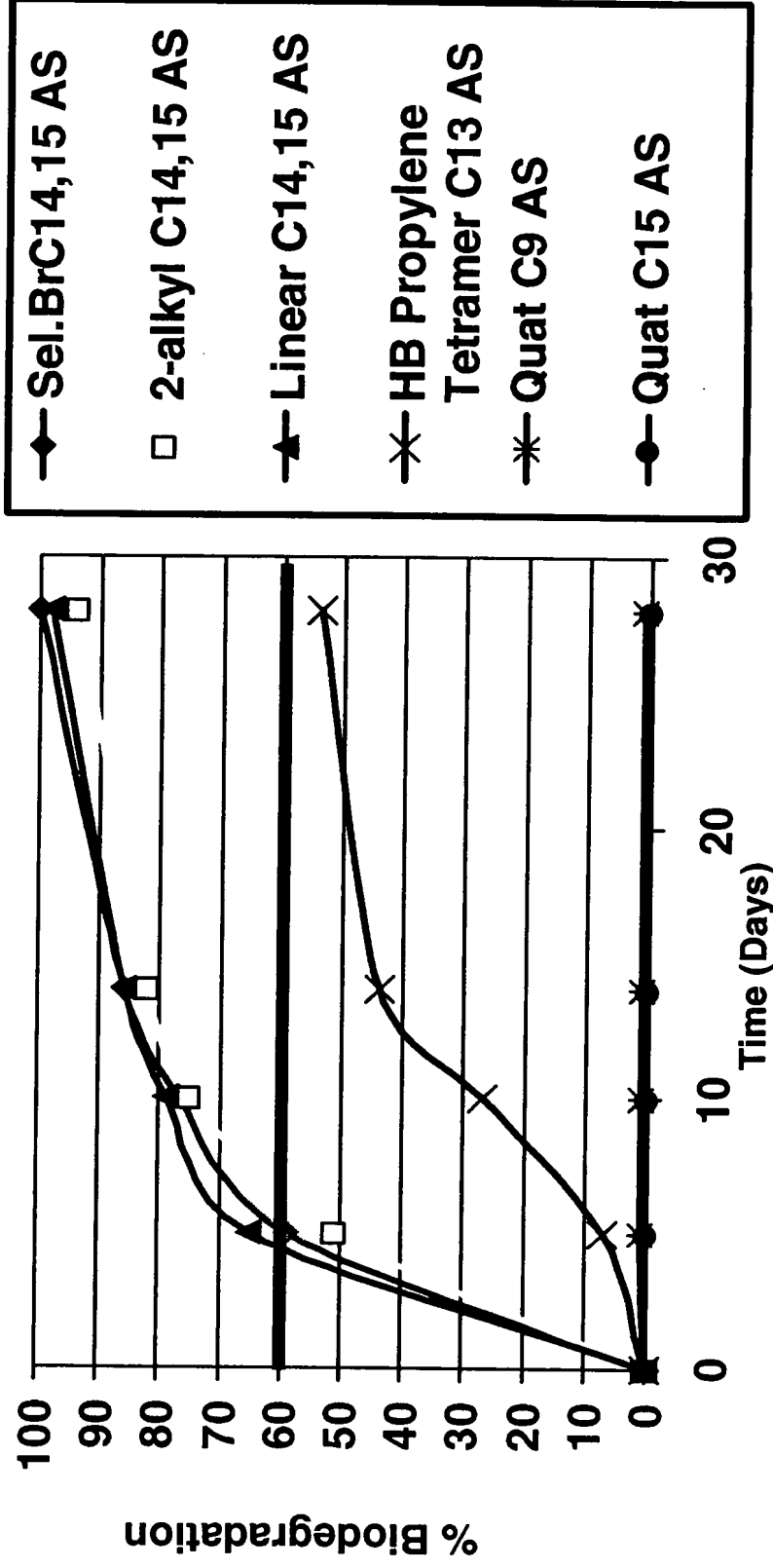
Shell Chemicals

Shell Hydroformylation Process

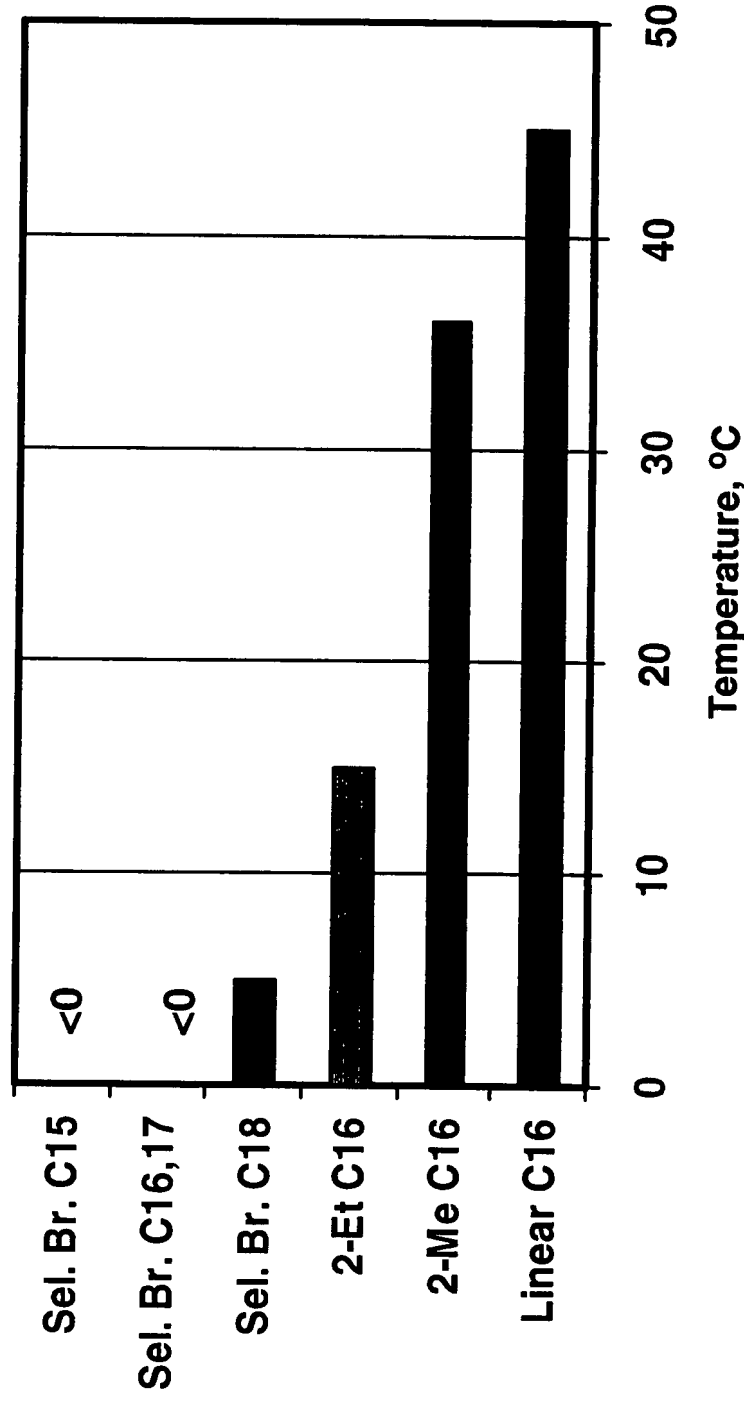


R distributed at desirable positions along backbone

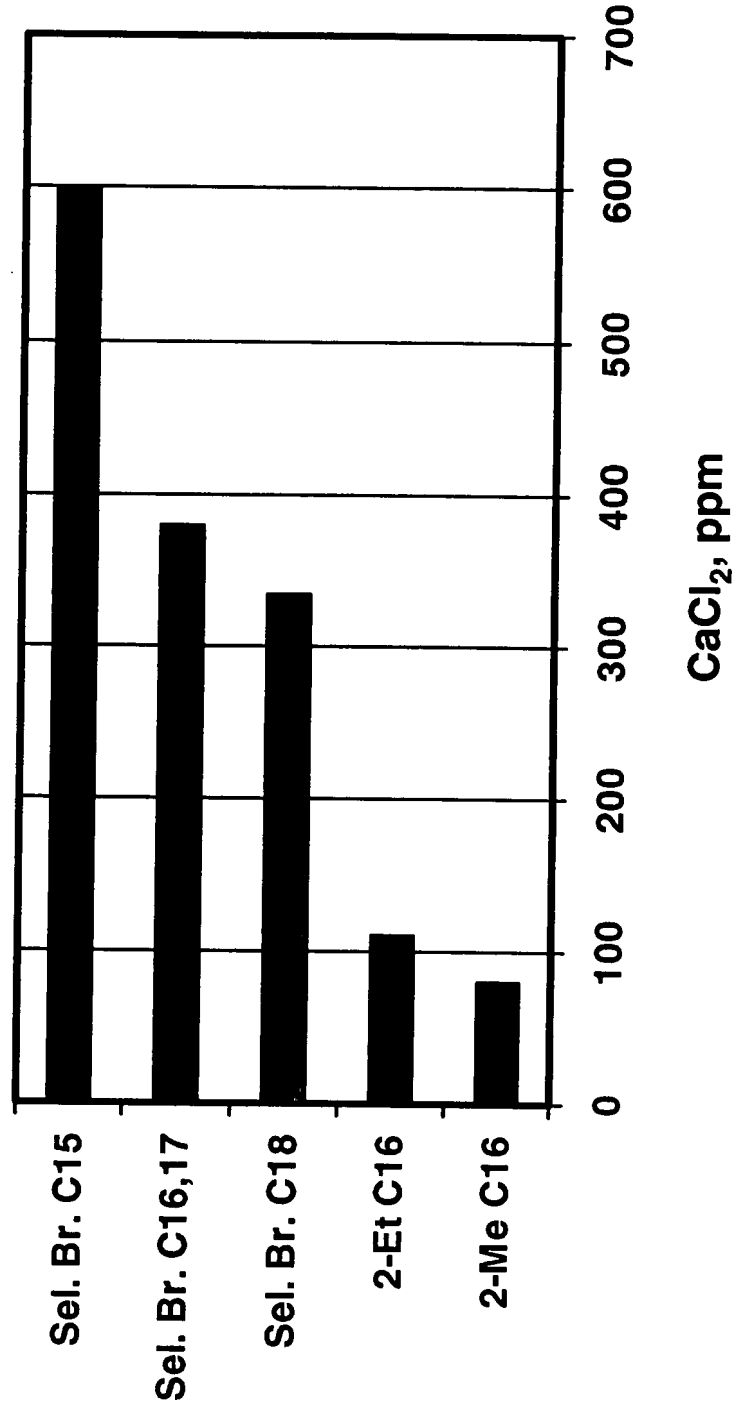
Closed Bottle Biodegradation Results for Various Alkyl Alcohol Sulfates



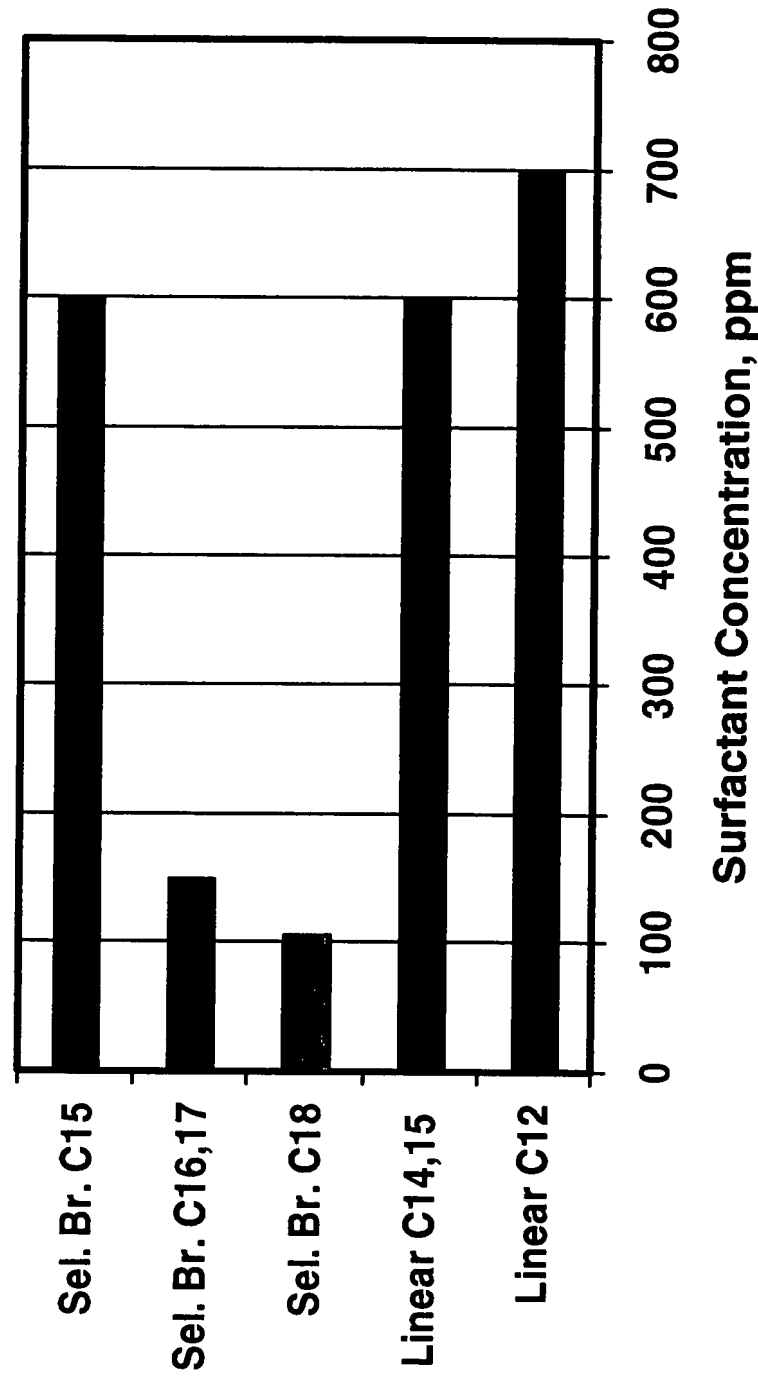
Krafft Temperature of the new Selectively Branched Alcohol Sulfates



Calcium Tolerance of the new Selectively Branched Alcohol Sulfates



Critical Micelle Concentration of the Selectively Branched Alcohol Sulfates

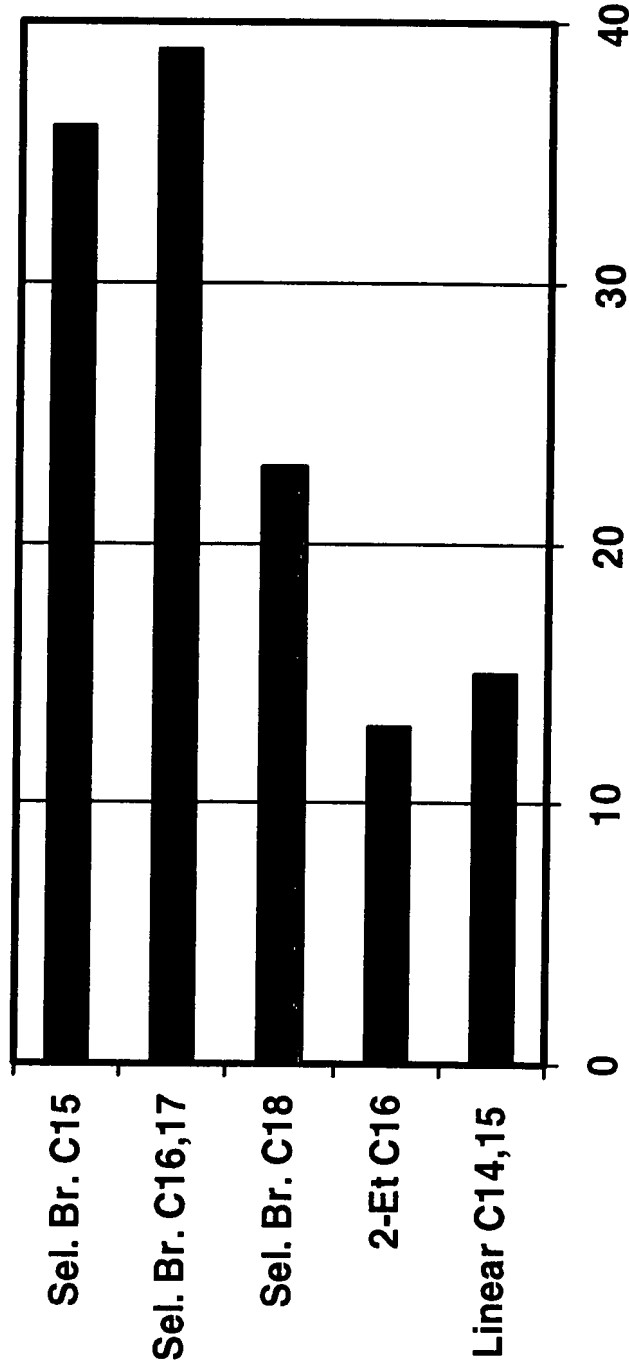




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Detergency Performance of the new Selectively Branched Alcohol Sulfates

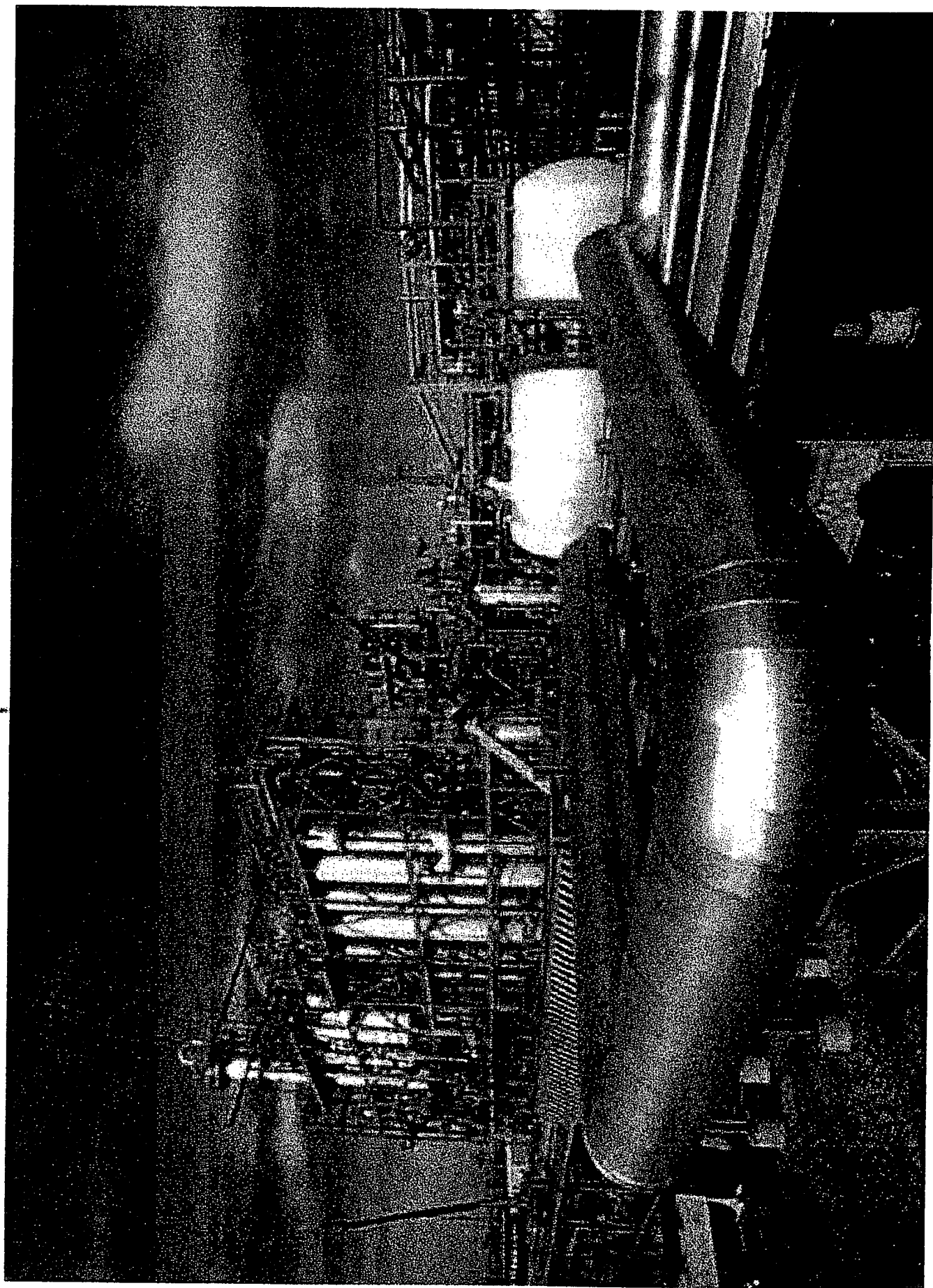
(at 10°C and 150 ppm Water Hardness)



% Soil Removal, $LSD_{95} = 4$

Partnering with Procter & Gamble

- P&G is a **Leading Global Supplier** to the Detergent Industry
- P&G conducted independent studies that pointed to a Primary Alcohol with a single methyl branch near the middle of the chain
- Evaluated various Shell “Selectively Branched” Alcohols
- Derivatized and formulated products based on the new alcohols
- A joint decision was made to commercialize the Innovation





Commercialization

- Product was scaled up in several stages (6, 50 and 3700 tonnes)
 - Allowed Process Modeling and Design Optimization
 - Customer feedback
- P&G worked closely with Shell during the Process
 - HS&E Studies, Alcohol Conversion and Product Formulation
 - Logistics, Product Specifications
 - Market Development Work
- World-Scale Olefin/Alcohol Plant built at Geismar, LA. in 2001
 - On spec product produced within 12 hours of feed-in
 - Breakthrough Technology Confirmed in Operations
- Alcohols successfully formulated into Quick Dissolving Tide®

“Tide is the most popular laundry detergent used in the USA”



New Opportunities

▪ Personal Skin Care Products

- Excellent Emollient / Moisturizer
- Non-oily
- Good Viscosity and Solubility Characteristics
- Biodegradable

▪ Industrial Fluids

- Low Pour Point
- Good Stability

▪ Chemical Intermediates

- Novel Composition
- Reagent for Various Industries



Acknowledgements

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W. Schmidt, T. Thomason
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 - D. Holecek, VP Technology – Americas
 - F. Keeth, President - Shell Chemical LP

Attachment 13



5th WORLD SURFACTANTS CONGRESS

May 29 - June 2, 2000
Fortezza da Basso
Firenze

FIRENZE

PROCEEDINGS

Volume 2



Comité Européen
des Agents de Surface

FEDERCHIMICA
Assobase - P.I.T.I.O.

Produttori Italiani
di Tensioattivi

SOLUTION AND PERFORMANCE PROPERTIES OF NEW BIODEGRADABLE HIGH-SOLUBILITY SURFACTANTS

W. Warren Schmidt, David M. Singleton, and Kirk H. Raney
Shell Chemicals

Abstract

Phase behavior, surface activity, and cleaning performance of biodegradable anionic and nonionic surfactant derivatives of long-chain alcohols have been studied. A tailored hydrophobe structure, which can be obtained through selective skeletal-isomerization of linear olefins followed by hydroformylation, provides enhanced cold-water solubility and improved water hardness tolerance as compared to conventional predominantly linear alcohol sulfates of comparable molecular weight. The impact of the structure on ethoxylated nonionic surfactant properties is less pronounced, although differences in physical properties such as pour point and gel formation are noted when compared to linear alcohol ethoxylates. Results of radiotracer detergency studies performed in a Terg-O-Tometer confirm the positive attributes of the high-solubility surfactants. This class of surfactant may permit advances in the consumer laundry process viewed from a full lifecycle perspective by enabling high cleaning performance under conditions favoring an improved environmental profile.

Résumé

Le comportement de phases, l'activité de surface et le pouvoir nettoyant des dérivés tensioactifs anioniques et non ioniques ont fait l'objet d'une étude. Une structure hydrophobe spécialement adaptée, qui peut être obtenue par l'intermédiaire de l'isomérisation squelettique des oléfines linéaires, suivie de l'hydroformylation, fournit une plus grande solubilité par temps froid et une meilleure tolérance de la dureté de l'eau, par rapport aux sulfates d'alcool conventionnels principalement linéaires dont le poids moléculaire est comparable. L'impact de la structure sur les propriétés des agents tensioactifs non ioniques éthoxylés est moins marqué, bien que des différences soient observées dans les propriétés physiques, telles que le point d'écoulement et la formation de gel, par rapport aux éthoxylats d'alcool linéaire. Les résultats des études de détergence au traceur radioactif effectuées dans un "Terg-O-Tometer" confirment les attributs positifs des agents tensioactifs de haute solubilité. Cette classe d'agents tensioactifs pourrait permettre de faire des progrès au niveau du processus de blanchissage de consommation, si on le considère du point de vue d'un cycle de vie complet, sous des conditions qui favorisent un meilleur profil environnemental.

Zusammenfassung

Es wurden Phasenverhalten, Grenzflächenaktivität und Reinigungsleistung biologisch zersetzbarer anionischer und nichtionisierender Tensidderivate untersucht. Eine genau abgestimmte wasserabweisende Struktur, die durch eine besonders gewählte Skelett-Isomerisierung linearer Olefins und einer nachfolgenden Hydroformylierung gebildet wurde, bietet eine erhöhte Kaltwasserlöslichkeit und bessere Wasserhärte-toleranz als herkömmliche und meistens lineare Alkoholsulfate eines vergleichbaren Molekulargewichts. Der Struktureinfluß auf die Eigenschaften ethoxylierter nichtionisierender Tenside ist weniger ausgeprägt, obwohl Unterschiede in den physikalischen Eigenschaften wie Pourpoint und Gelbildung im Vergleich mit linearen Alkoholethoxylaten zum Vorschein kommen. Mit den Ergebnissen von Radionuklid-Untersuchungen in einem Terg-O-Tometer wurden die positiven Merkmale der Tenside mit hoher Löslichkeit bestätigt. Aus der Sicht einer Voll-Lebenskreislauf-Perspektive unter Bedingungen, die ein verbessertes Umweltsprofil begünstigen, kann diese Tensidgruppe zu einem Fortschritt des Verbraucher-Wäschereiprozesses führen.

INTRODUCTION

Branched alcohols are an important constituent of many high volume synthetic detergent alcohols made using the Oxo process (1). In separate work, it was shown that the separated branched fraction of certain synthetic alcohols exhibited an excellent biodegradation profile (2). It was obviously of interest to document the effect of specific alcohol branching on the surfactant properties of alcohol sulfates. Additionally, random mono-methyl alcohols were synthesized, and physical chemistry and laboratory cleaning evaluations conducted.

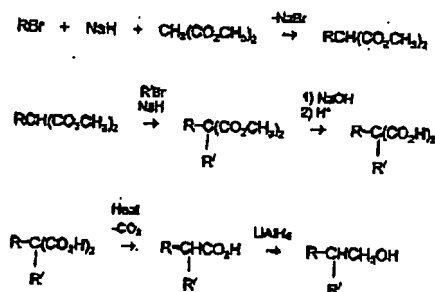
Early German workers used laboratory organic synthesis to make a limited series of alcohols and sulfates (3). For this research, two versatile synthetic schemes were adapted to a wide range of compounds, and the performance testing was likewise modified to reflect current practice including lower wash temperatures.

EXPERIMENTAL

General Methods for Synthesis: As depicted in Figure 1, a variety of alcohols were synthesized by

Figure 1

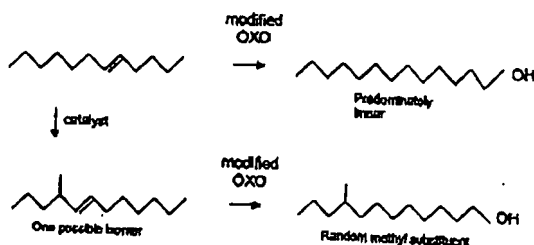
Malonic Ester Synthesis of 2-Alkyl Branched Alcohols



alkylation of malonic ester (4). With this method, alcohols with a total of C-12 to C-18 were made, and 2-alkyl branches from C-1 to C-6 were incorporated. Figure 2 shows the two-step procedure for introducing random mono-methyl branching into an alcohol (5). The alcohols were > 97% pure. All CISO_3H , followed by neutralization with NaOH (6).

Figure 2

Random Methyl Alcohol Synthesis



Krafft Temperatures of Alcohol Sulfates: Aqueous 1% surfactant solutions were frozen, and the solutions were allowed to slowly warm. The reported Krafft temperature is the temperature where the solution was fully transparent.

Calcium Tolerance: Aqueous surfactant solutions were made at a concentration of 0.06% weight, and adjusted to a pH of approximately 9 with 1% NaOH. The surfactant solutions were warmed to 40 °C. Aliquots of 10% CaCl₂ were added, and the surfactant which remained dissolved in the upper (clear) layer was determined via the two phase titration method (7). The reported calcium tolerance is amount of CaCl₂ which must be added to precipitate 50% of the anionic surfactant.

The random mono-methyl C-16,17 alcohol was ethoxylated with an average of nine ethylene oxide groups using standard KOH ethoxylation. For comparison, a nine-EO ethoxylate with a linear C-16 hydrophobe was prepared by blending ethoxylates obtained from Uniqema. Also studied were the seven-EO ethoxylates obtained through standard ethoxylation of the linear and branched fractions of a predominately linear C-14,15 alcohol.

The cloud point and Krafft temperature of 1% aqueous alcohol ethoxylate solutions were measured in deionized water using dipping probe turbidimetry (8,9). Solutions were first chilled overnight in a freezer at -5°C. The solutions were then heated at a rate of about 1°C/minute in a jacketed beaker with agitation provided by a Glas-Col® non-aerating stirrer at 3000 rpm. Turbidity was determined by measuring the light transmittance through the solution at 650 nm. The first temperature where complete clearing of the solution occurred was taken as the Krafft temperature while the higher temperature at which turbidity reappeared due to formation of a dispersed phase was taken as the cloud point.

Solution Time Method: The solution times of the neat ethoxylates were measured by injecting 0.20 cc of liquid surfactant into 50 cc deionized water in a flat bottom pour point tube (Coming No. 6900). The water was stirred at 500 rpm with a 1.5 cm x 0.5 cm magnetic stirring bar. The times for complete surfactant dissolution were measured at 25°C with the temperature of the sample being controlled by placing the pour point tube in a thermostatically-controlled water bath. Measurements were performed in duplicate and averaged.

Alcohol Ethoxylate Pour Points: Pour points for the commercial C-14,15 samples were obtained using method ASTM D97-85 with an automatic pour point apparatus. Visual determination of pour points was made for the other samples by observing their flow behavior as 50 cc were slowly warmed in a water bath.

Surface Tension: Equilibrium surface tension as a function of surfactant concentration was measured at 25°C using an automated Lauda tensiometer. This instrument doses fixed increments of stock solution into 100 cc of deionized water that is contained in a thermostatically-controlled beaker. Equilibrium surface tension is measured automatically using the Du Nuoy ring method. From the surface tension-concentration plots, critical micelle concentration was determined by standard procedures (10).

Detergency: Multisebum soil removal was determined using the published laboratory radiotracer detergency procedure (11,12). All alcohol sulfates were evaluated in the following prototype formulation: 0.2 g/L anionic, 0.34 g/L zeolite, and 0.2 g/l of Na₂CO₃.

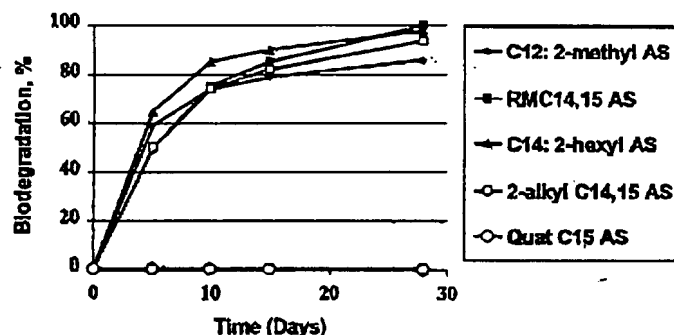
Biodegradation: A laboratory estimation of biodegradation was conducted by an adaptation of the CO₂ evolution method of Sturm (13)

DISCUSSION

• Biodegradation

A screening study of biodegradation was used to compare a variety of alcohol sulfates. As depicted in Figure 3, only a surfactant synthesized to contain a quaternary carbon atom failed to evolve CO₂ at a

Figure 3
Closed Bottle Biodegradation Results for 2-Alkyl Alcohol Sulfates



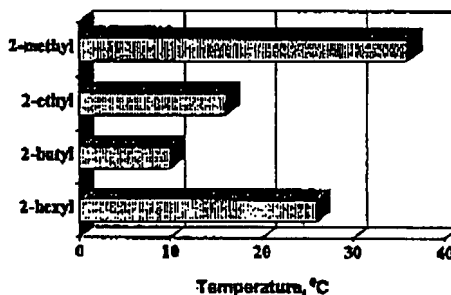
rapid rate. A variety of 2-alkyl branches or a random mono-methyl substituent all performed equally well in this screen. This result was at least in part predicted by the previous work from Shell (2).

• Surfactant Properties of 2-Alkyl Alcohol Sulfates

Displayed in Figure 4 are the Krafft temperatures of branched C-16 alcohol sulfates. With this series of alcohol sulfates, the minimum in Krafft temperature occurs with the attachment of a 2-butyl group. The all linear hexadecanol sulfate has a Krafft temperature of 45 °C (14).

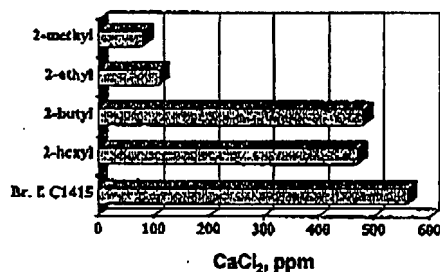
Figure 4

Krafft Temperature of C16: 2-Alkyl Branched Alcohol Sulfates



The calcium tolerance of this series of C-16 alcohol sulfates is depicted in Figure 5. The methyl and ethyl derivatives are approximately equal, while either butyl or hexyl introduce the greatest solubility.

Figure 5
Calcium Tolerance of C16; 2-Alkyl
Alcohol Sulfates

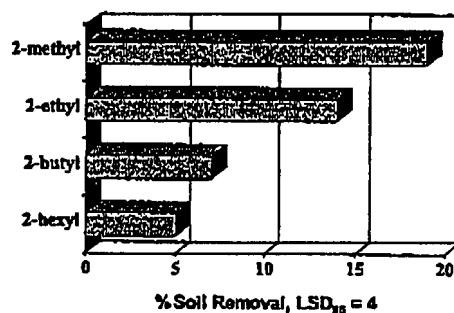


- Detergency Evaluation of 2-Alkyl Alcohol Sulfates

In 1969 Götte and Schwuger (3) reported the reflectance detergency of branched C-16 alcohol sulfates at 40 °C. It was noted that the 2-methyl branched alcohol sulfate gave the highest level of cleaning. With the availability of a broader selection of chain lengths, the generality of this observation has been investigated.

In this present work, C-16 alcohol sulfates were evaluated at 10 °C by an alternative radiotracer

Figure 6
Multisebum Detergency of C16 Alcohol
Sulfates: 10 °C and 150 ppm Water
Hardness



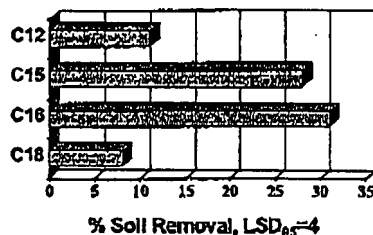
method, see Figure 6. Despite having the highest Krafft temperature and the lowest calcium tolerance, the 2-methyl derivative is the best performer, as observed by Götte and Schwuger (3). It is remarkable that the pattern was the same, since the temperature, soil, builder, and formulation are all different. This excellent activity is probably the result of greater surface activity of the 2-methyl surfactant. However, it is likely that the surfactant did not fully dissolve at the detergency conditions used here.

Additionally, a variety of total chain lengths, all with 2-methyl branches were evaluated, Figure 7. Performance is optimized for the C-16 total chain length, at the low temperature cleaning conditions utilized. It is presumed that the C-12 derivative has a relatively high cmc, and thus more surfactant would have been required. The C-18 material was poorly soluble, and therefore little surfactant was available at the conditions of this evaluation.

These surface chemistry and cleaning studies suggested that the length of the branch was an important variable in hydrophobe optimization. Exploratory chemistry yielded a way to synthesize alcohols with nearly exclusively methyl substituents (5).

Figure 7

Detergency Performance of 2-Methyl Branched Alcohol Sulfates 10 °C and 150 ppm Hardness

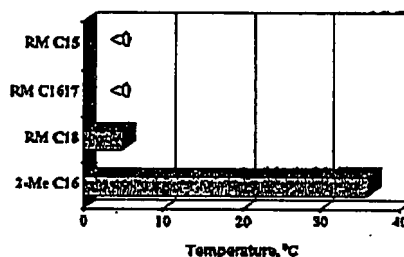


• Surfactant Properties of Random Methyl Alcohol Sulfates

Shown in Figures 8 and 9 are surfactant properties as a function of carbon content for the random methyl branched alcohol sulfates. Excellent cold water solubility is exhibited by all three RM samples

Figure 8

Krafft Temperature of RM Branched Alcohol Sulfates



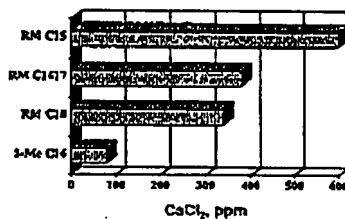
better
solubility
than

C2 branched
only

as compared to pure 2-Me C16 alcohol sulfate which is not fully soluble at 1% concentration until heated to 36°C. Also, as shown in Figure 9, the random methyl systems exhibit much higher calcium tolerance than the 2-Me C16 alcohol sulfate.

Figure 9

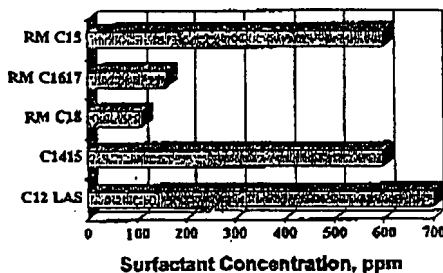
Calcium Tolerance of RM Branched Alcohol Sulfates



Critical micelle concentration values in deionized water for the RM sulfates at 25°C are compared in Figure 10 to values for a predominantly linear C1415 alcohol sulfate and C12 LAS. As expected, the RM alcohol sulfates having a high molecular weight exhibit quite low cmc's, indicative of low dosing requirements in laundry processes. Nevertheless, their Krafft temperatures are much lower than that for the commercial C1415 linear alcohol sulfate (37°C), and their calcium tolerance is much higher than

those for the C1415 sulfate and C12LAS, which are 40 ppm and 140 ppm, respectively. All three

Figure 10
Critical Micelle Concentration of RM
Branched Alcohol Sulfates

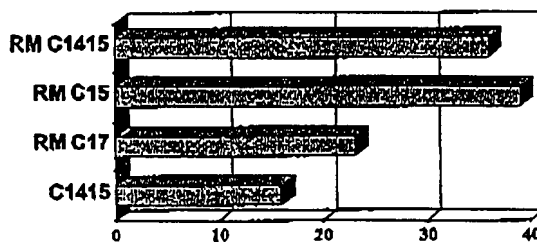


factors, low Krafft temperature, high calcium tolerance, and low cmc, are positive attributes of the random methyl alcohol sulfates which should contribute to excellent detergent properties, particularly in underbuilt systems at low washing temperatures.

- Detergency Evaluation of Random Methyl Alcohol Sulfates

Three different random-methyl alcohol sulfates were compared to a linear C-14,15 alcohol sulfate, Figure 11. Each of the randomly substituted alcohol sulfates was superior to the comparison surfactant.

Figure 11
Detergency Performance of RM Branched
Alcohol Sulfates
10 °C and 150 ppm Hardness



*better
detergency*

Random Methyl and 2-Alkyl Ethoxylates

Shown in Table 1 are the results for the tested ethoxylates. For a given average hydrophobe weight, the presence of branching resulted in modest reductions in pour point and an increase in critical micelle concentration. Interestingly, a Krafft temperature phenomenon was noted in the linear systems which is atypical for nonionic surfactant systems. These systems exhibit decreased solubility both at low temperatures due to crystallinity and at high temperatures where EO dehydration results in phase separation above the cloud point temperature. In contrast, no crystallization occurred at 1% concentration for the branched analogues, i.e., the Krafft temperatures for these systems were below zero. The lower solubility in cold water exhibited by the linear ethoxylates also contributes to the much slower rates of dissolution observed for these systems at 25°C as compared to the respective branched ethoxylates.

Table 1

Physical and Solution Properties of Branched and Linear Alcohol Ethoxylates

Surfactant	Pour Point (°C)	Cloud Point (°C)	Krafft Temperature (°C)	Dissolution Time (min.)	Critical Micelle Concentration (ppm)
C14,15-7 (linear)	24	50	25	21	3
2-alkyl-C14,15-7	10	a)	<0	8	5
C16-9 (linear)	32	63	35	>120	1
RAM C16,17-9	21	50	<0	33	2

a) solution was slightly turbid between 0 and 40°C resulting in no distinct cloud point

CONCLUSIONS

The surfactant properties and detergency performance of model 2-alkyl alcohol sulfates have been examined. Addition of a 2-alkyl group reduces the Krafft temperature; improves the calcium tolerance, and the surfactants biodegrade readily.

Additionally:

- laboratory synthesis methods have been developed to prepare random mono-methyl alcohols, which are readily converted to either sulfates or ethoxylates;
- both specific 2-alkyl and random mono-methyl substituents improve the physical chemistry properties of the corresponding alcohol sulfates;
- solubility enhancements are likewise observed for alcohol ethoxylates containing the same branched hydrophobes; and,
- both 2-alkyl branched alcohol sulfates and random mono-methyl sulfates clean well, particularly at cool wash temperatures.

It is expected that a full environmental profile for random methyl substituted surfactants would be favorable: excellent biodegradation is expected, and the combination of good solubility and low sensitivity to water hardness should translate into the ability to wash at lower water temperatures.

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Attachment E



Shell Chemicals

Detergency Performance of the New Selectively Branched Alcohol Sulfates

(at 10°C and 150 ppm Water Hardness)

